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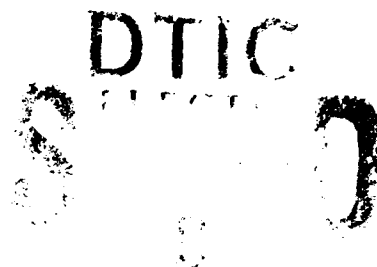


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Molecular Engineering of Liquid Crystal Polymers by Living
Polymerization. 17. Characterization of Poly{ 10-[(4-Cyano-4'-Biphenyl)
oxy]decanyl Vinyl Ether}s by 1-D and 2-D ¹H-NMR Spectroscopy

by

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SUMMARY

The characterization of poly{10-[(4-cyano-4'-biphenyl)oxy]decanyl vinyl ether} obtained by living cationic polymerization initiated with $\text{CF}_3\text{SO}_3\text{H}/\text{S}(\text{CH}_3)_2$ in CH_2Cl_2 at 0°C and terminated by ammoniacal methanol, by 1-D and 2-D (COSY) 300 MHz ^1H -NMR spectroscopy is presented. The polymer contains one methyl and one methoxy chain ends, thus, demonstrating the absence of chain transfer and termination reactions. The number average degree of polymerization determined from the ^1H -NMR spectrum agrees with the one expected from the $[\text{M}]_0/[\text{I}]_0$ ratio.

Keywords: living cationic, chain ends, 2-D ^1H -NMR spectroscopy.

INTRODUCTION

Since the first examples of mesogenic vinyl ethers and liquid crystalline poly(vinyl ether)s were reported from our laboratory (1), several research groups became actively engaged in the synthesis of liquid crystalline poly(vinyl ether)s mainly because they can be polymerized by living cationic mechanism (2,3,4). So far, we have elucidated the influence of molecular weight on the phase transitions of poly{ ω -[(4-cyano-4'-biphenyl)oxy]alkyl vinyl ether}s with alkyl groups from ethyl to undecanyl (5). Binary copolymerization experiments performed with the same monomers at constant copolymer molecular weight allowed the molecular design of nematic, smectic A and reentrant nematic mesophases (6). Similar homopolymerization and copolymerization experiments were used to tailor make polymers exhibiting a chiral smectic C mesophase (7). In addition, it has been shown that many functional mesogenic vinyl ethers (8) can be polymerized by our preferred initiating system $\text{CF}_3\text{SO}_3\text{H}/\text{S}(\text{CH}_3)_2$ in CH_2Cl_2 (9).

The experiments described so far (5-8) required only a good control over the degree of polymerization and polydispersity of the polymer. In order to synthesize more complex architectures derived from liquid crystalline poly(vinyl ether)s we have to control in a quantitative manner the nature of the polymer chain ends. This has been shown to be possible with polymers derived from alkyl vinyl ethers (10). The simplest avenue available to check the capability to functionalize the chain ends of poly{ ω -[(4-cyano-4'-biphenyl)oxy]alkyl vinyl ether}s is by providing a quantitative analysis of the polymer obtained after termination with ammoniacal methanol. This communication describes the characterization of poly{10-[(4-cyano-4'-biphenyl)oxy]decanyl vinyl ether} by 1-D and 2-D 300 MHz ^1H -NMR spectroscopy.

EXPERIMENTAL

The synthesis of poly{10-[(4-cyano-4'-biphenyl)oxy]decanyl vinyl ether} (6-10), its living cationic polymerization initiated with $\text{CF}_3\text{SO}_3\text{H}/\text{S}(\text{CH}_3)_2$ in CH_2Cl_2 at 0°C and the characterization of the resulted polymers were presented in a previous publication from our laboratory (5d).

The 1-D ^1H and 2-D ^1H -NMR (COSY) spectra were recorded at 299.55 MHz on a VXR-300 NMR spectrometer equipped with a 5 mm indirect detection probe in CDCl_3 at room temperature. 1-D spectra were obtained with a 5,600 Hz spectral width, 2.926 s acquisition time, 4 μs 130° pulse, 0 s relaxation delay and 2,048 transients. The

2-D ^1H -NMR (COSY) spectra were obtained with a 2,775.5 spectral width, 0.184 s acquisition time, 13 μs 90° pulse, 1 s delay between transients and 32 transients.

RESULTS AND DISCUSSION

Poly{10-[(4-cyano-4'-biphenyl)oxy]decanyl vinyl ether} (6-10) with a theoretical degree of polymerization of four and $M_w/M_n=1.15$ was synthesized by initiation with $\text{CF}_3\text{SO}_3\text{H}/\text{S}(\text{CH}_3)_2$ in methylene chloride at 0°C. The polymerization was terminated by methanol containing ammonia. Details of this polymerization were presented previously (5d). The ideal structure of poly(6-10) resulted from this living polymerization reaction is shown in Scheme 1. Scheme 2 outlines the structure of the chain ends expected to result from the chain transfer to monomer and counter anion and from termination reactions.

Figure 1 shows the 1-D ^1H -NMR spectrum of poly(6-10) together with its proton assignments. 2-D ^1H -NMR spectrum is presented in Figure 2. The aromatic region of the poly(6-10) is presented in Figure 2a while the aliphatic part of the same spectrum in Figure 2b. The off-diagonal cross-peaks from Figure 2a,b indicate which protons are J-coupled and support the assignment of proton resonances from Figure 1. The chemical shifts of these assignments are summarized in Table 1. The signals due to the methyl (signal a), methoxy (signal f) and acetal $-\text{CH}_2(\text{O})\text{CHO}-$ (signal e), chain ends were integrated. Their experimental ratios (i.e., $f/a=1$ and $a/e\approx 3.0$) correspond to the theoretical values expected for a polymer resulted from a polymerization free of chain transfer and termination reactions (Table II). The calculated degree of polymerization ($\text{DP}=n/2e=3.4$) is very close to the theoretical one i.e., $[\text{M}]_0/[\text{I}]_0=4.0$.

In addition, the NMR spectra of this polymer do not show any unsaturated chain ends which would result from chain transfer reactions. Only a very small signal at 9.8 ppm can be observed. This signal is due to a $-\text{CHO}$ chain end which results from the termination reaction. However, it represents less than 1% of the total concentration of the methoxy chain end. The ^1H -NMR spectra of poly(6-10)s with degree of polymerization up to 30 were analyzed and show the same behavior. These results demonstrate that a quantitative functionalization of the poly(6-10) prepared with this initiation system is possible and that the absolute number average molecular weight of the polymers with degrees of polymerization up to 30 can be determined by ^1H -NMR spectroscopy (7).

ACKNOWLEDGMENTS

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FIGURES AND SCHEME CAPTIONS

Figure 1: 300 MHz 1-D ^1H -NMR spectrum of poly{10-[(4-cyano-4'-biphenyl)oxy]decanyl vinyl ether} with theoretical degree of polymerization of 4.

Figure 2: 2-D ^1H -NMR (COSY) spectrum of poly{10-[(4-cyano-4'-biphenyl)oxy]decanyl vinyl ether} with theoretical degree of polymerization of 4: a) aromatic region; b) aliphatic region.

Scheme 1: The ideal structure of poly{10-[(4-cyano-4'-biphenyl)oxy]decanyl vinyl ether} obtained by living polymerization initiated with $\text{CF}_3\text{SO}_3\text{H}/\text{S}(\text{CH}_3)_2$ and terminated with ammoniacal methanol.

Scheme 2: Chain transfer and termination reactions.

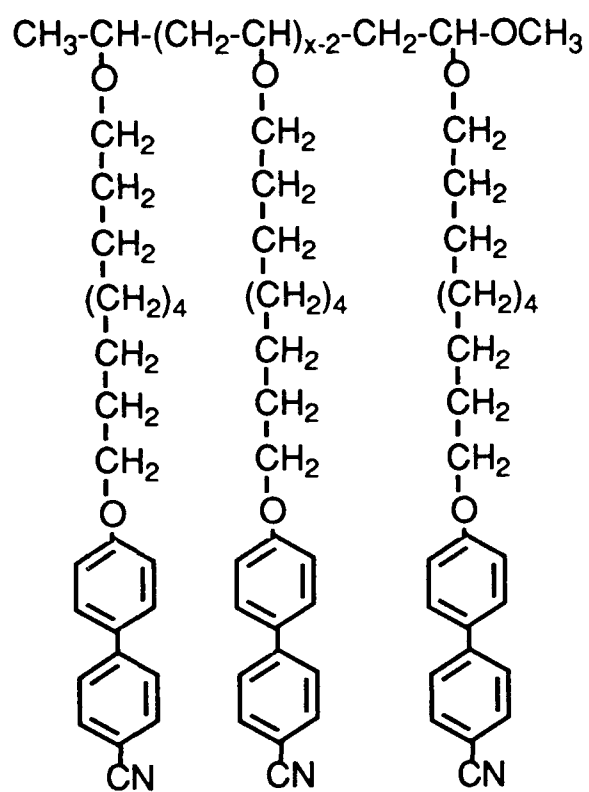
Table I. ^1H -NMR Chemical Shifts of Poly(6-10)

proton	label	chemical shift (ppm)	nature of signal
polymer backbone	a	1.12	d
	b	3.50	m
	c	1.75	m
	d	1.75	m
	e	4.60	m
	f	3.30	s
flexible spacer	g	3.43	m
	h	1.53	m
	i	1.42	m
	j	1.29	m
	k	1.44	m
	l	1.78	m
	m	3.90	t
aromatic region	n	6.94	d
	o	7.47	d
	p	7.65	d of d
	q	7.65	d of d

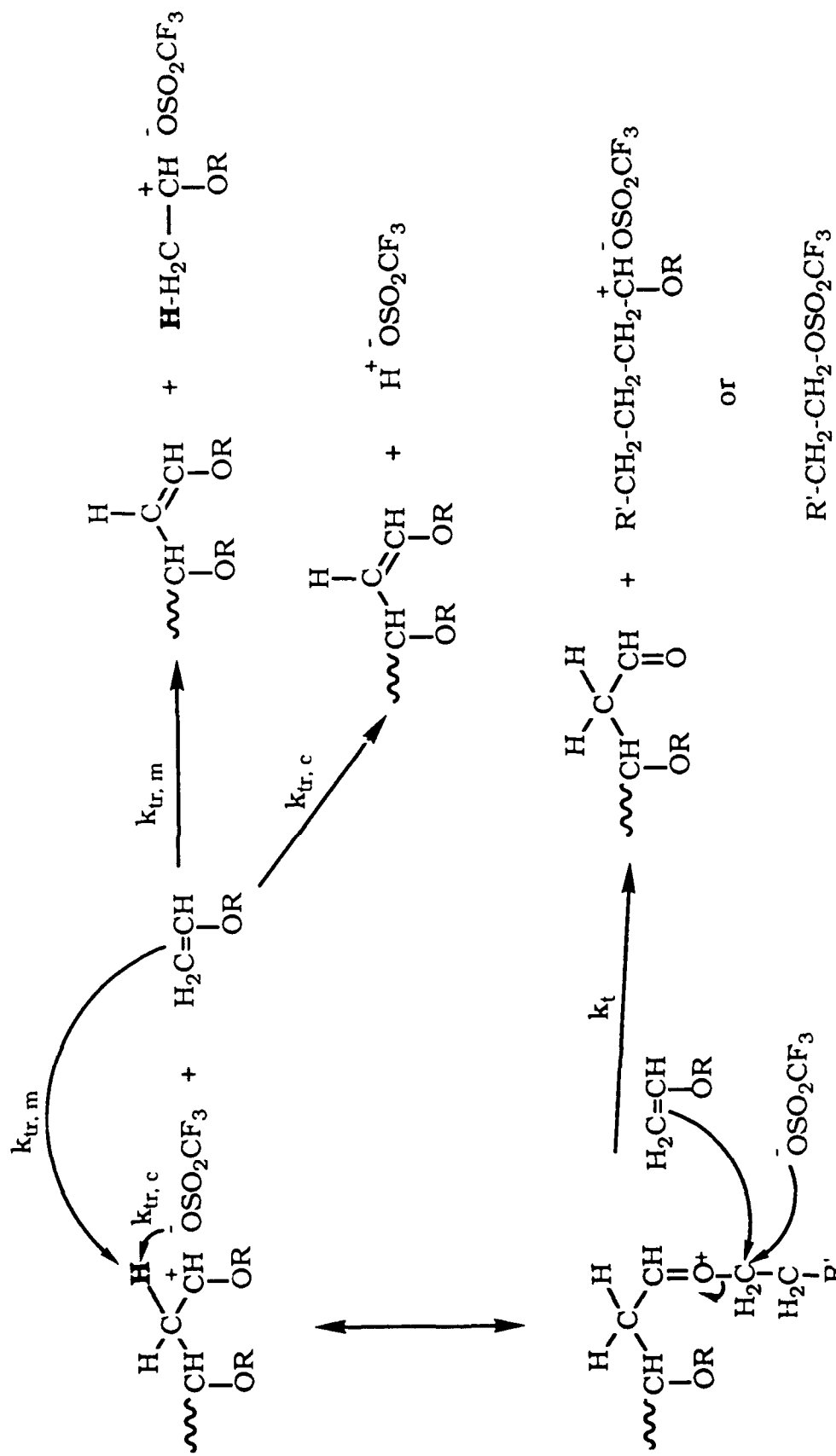
Table II. Integration Ratio of Polymer Chain Ends

proton	integration ratio (NMR)	theoretical ratio
f/a	0.96 ^a	1.0
n/e	6.80 ^b	8.0
a/e	2.87	3.0

^a Number of methoxy end groups/polymer chain^b DP (NMR)=6.8/2=3.4



Scheme 1



Scheme 2

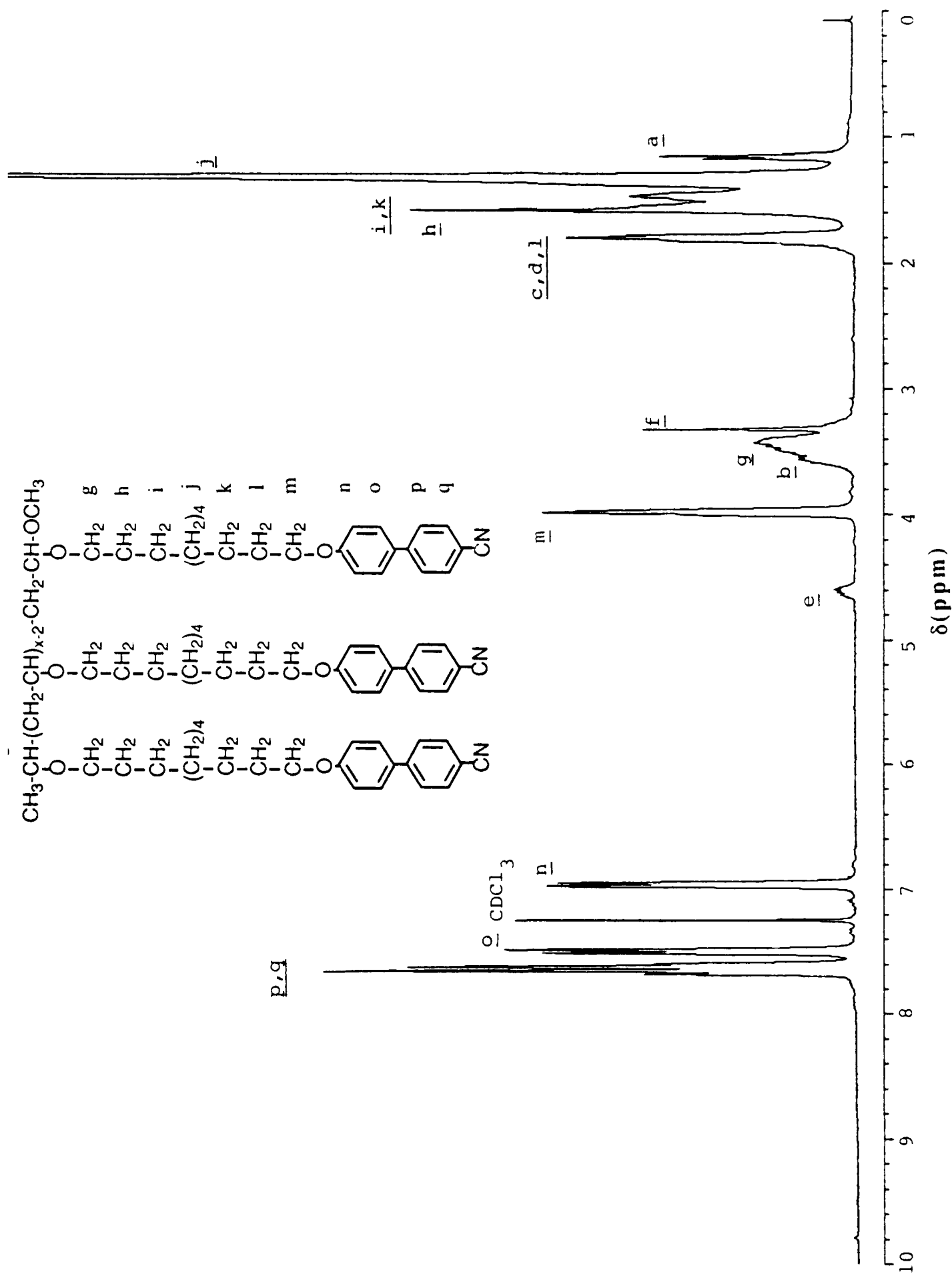


Figure 1

Figure 2a

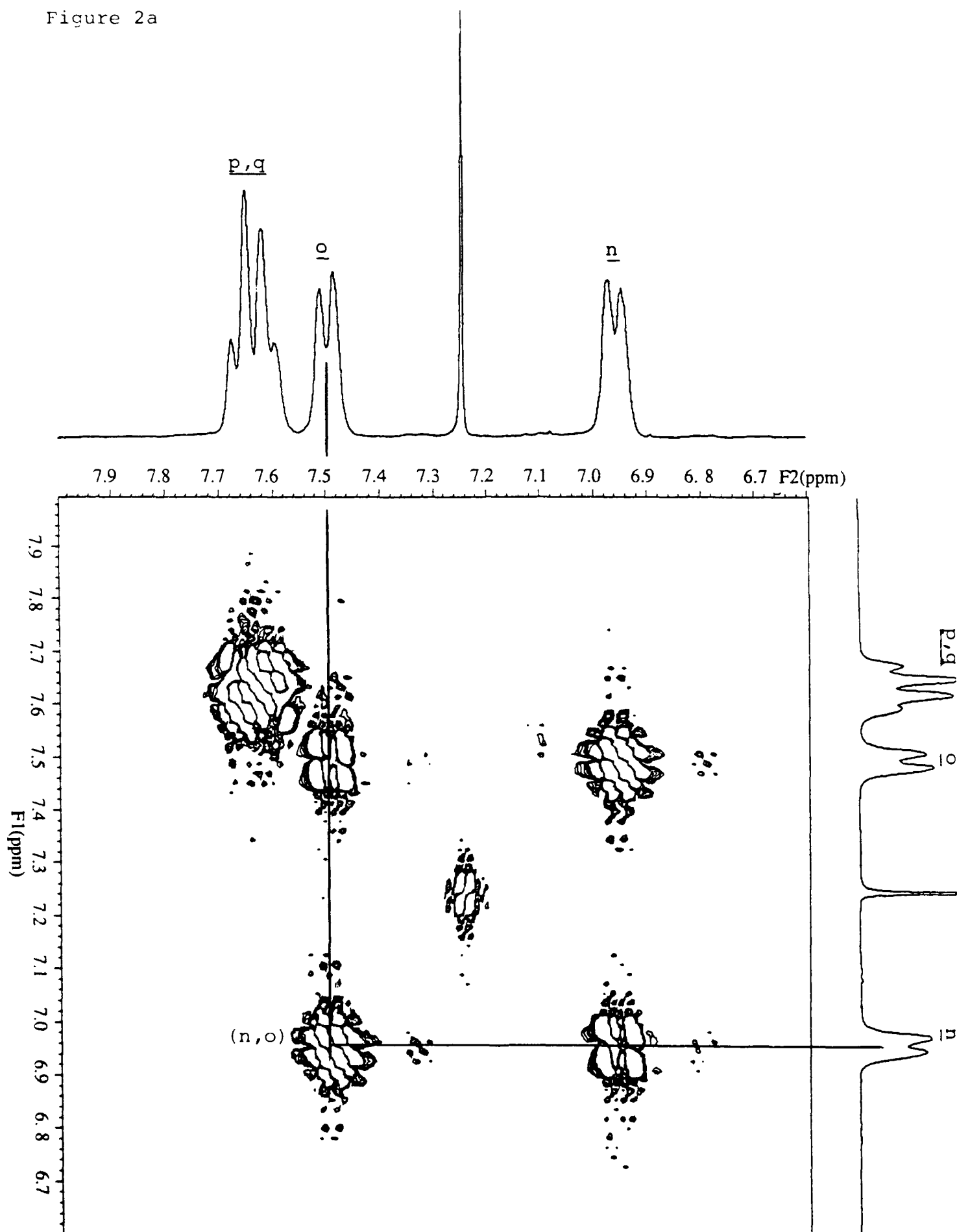


Figure 2b

